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Design and testing of sorbents for CO2 separation of post-combustion and natural gas sweetening applications

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SORBENT DESIGN AND TESTING FOR CO_2 SEPARATION FOR POST-COMBUSTION AND NATURAL GAS SWEETENING APPLICATIONS

CO_2 SUMMIT II: TECHNOLOGIES AND OPPORTUNITIES

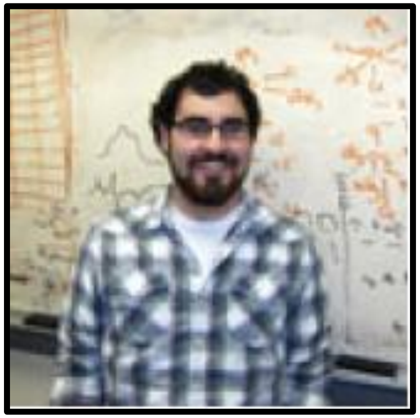
APRIL 10-14, 2016

SANTA ANA PUEBLO, NEW MEXICO

JENNIFER WILCOX

The Team – Coupled Experiments and Theory

Synthesis, Characterization, Testing and Monte Carlo



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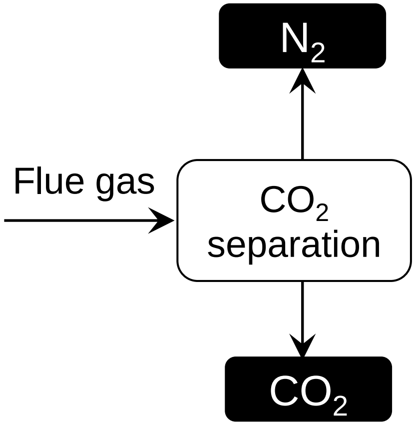
Objectives

- Develop porous carbons targeting specific CO_2 capture processes
- Optimize the carbon properties for enhanced capture performance
- Investigate the roles of the sorbent's textures and functionalities in the capture performance

Post-combustion capture[1]



Flue gas

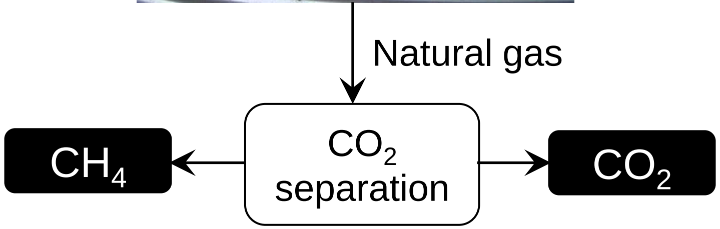
CO_2 separation

N_2

CO_2

- Low CO_2 partial pressures
- Trace acid gas (SOx, NOx, etc.)

Natural gas sweetening



Natural gas

CO_2 separation

CH_4

CO_2

- High CO_2 partial pressures
- Sometimes contains H_2S

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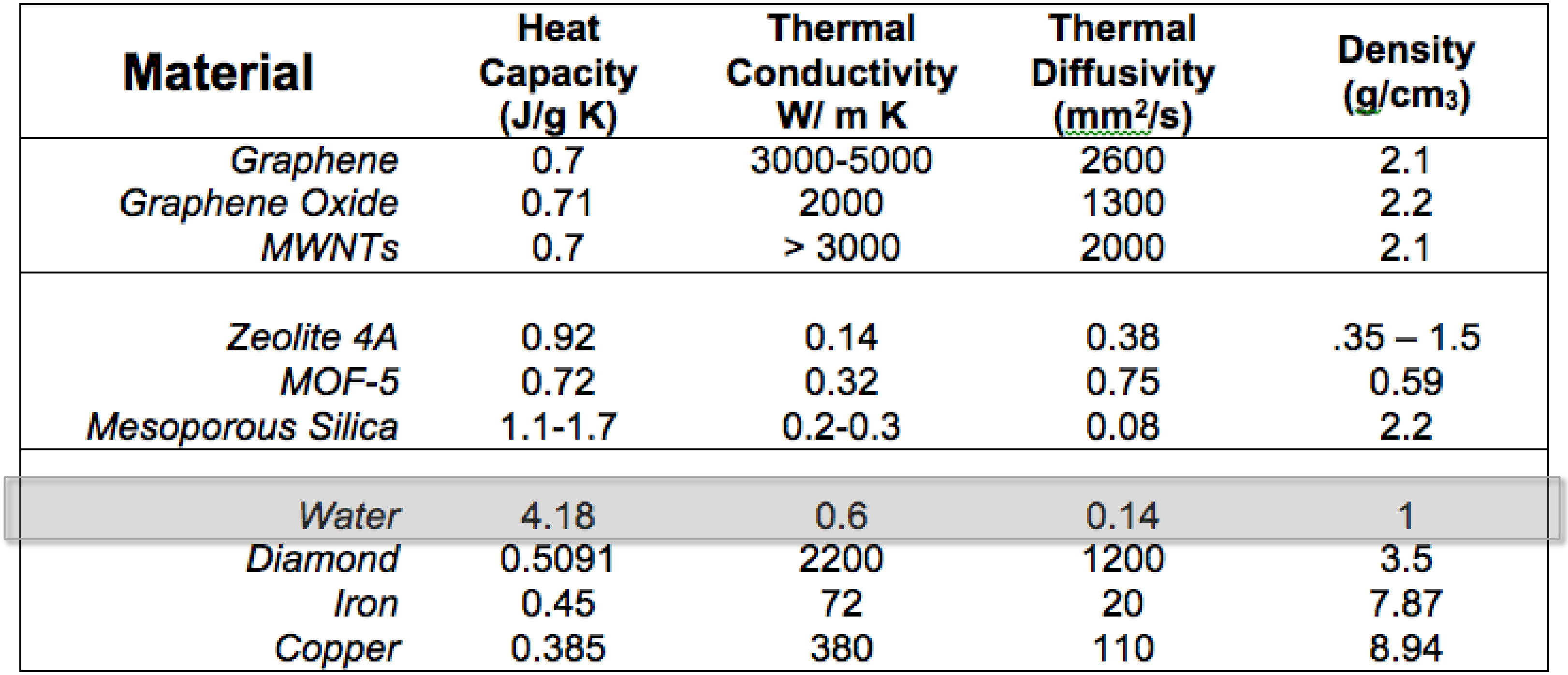
[1] To et al., J. Amer. Chem. Soc., 2015

Closer Look at Heat Properties



Material	Heat Capacity (J/g K)	Thermal Conductivity W/ m K	Thermal Diffusivity (mm^2/s)	Density (g/cm$_3$)
Graphene	0.7	3000-5000	2600	2.1
Graphene Oxide	0.71	2000	1300	2.2
MWNTs	0.7	> 3000	2000	2.1
Zeolite 4A	0.92	0.14	0.38	.35 – 1.5
MOF-5	0.72	0.32	0.75	0.59
Mesoporous Silica	1.1-1.7	0.2-0.3	0.08	2.2
Water	4.18	0.6	0.14	1
Diamond	0.5091	2200	1200	3.5
Iron	0.45	72	20	7.87
Copper	0.385	380	110	8.94

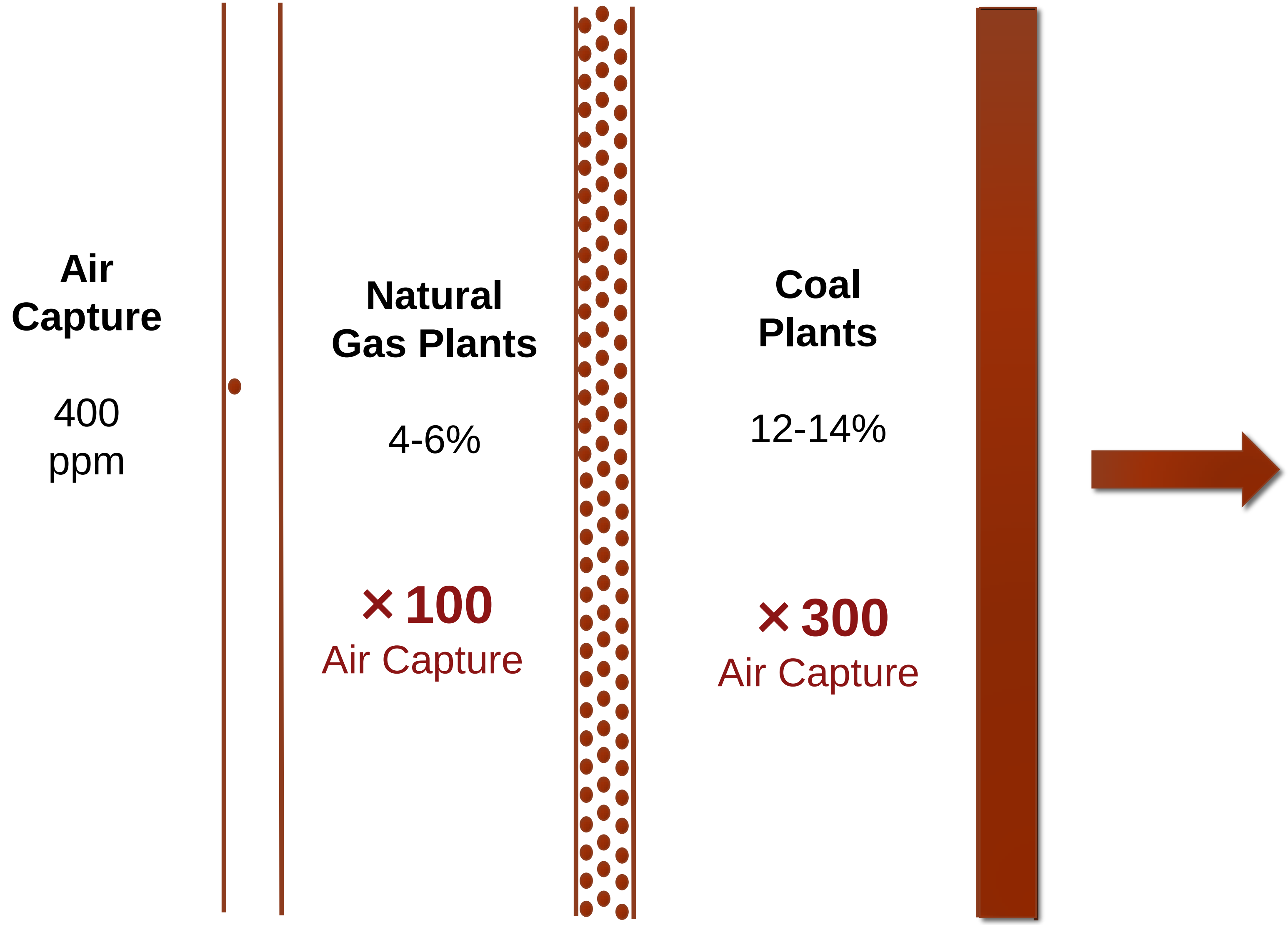
Assume:

Heat of regeneration = $C_p\Delta T + \Delta H$

heating up all material in system from T_1 to T_2 + breaking the CO_2 interaction

Sorbent Design Depends on Application

optimal pore size depends upon dilution



Air Capture

400 ppm

Natural Gas Plants

4-6%

× 100

Air Capture

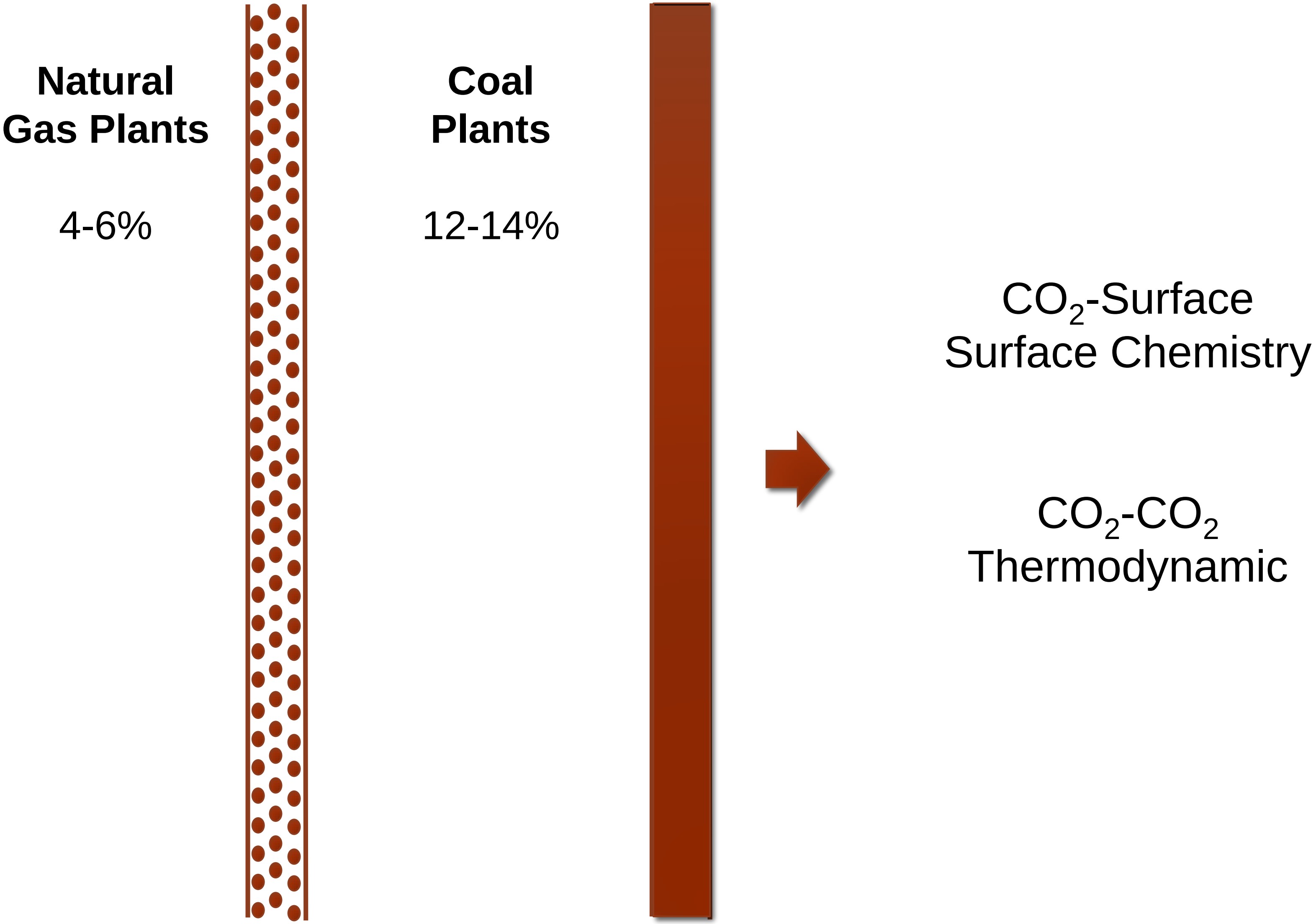
Coal Plants

12-14%

× 300

Air Capture

2 Mechanisms Impacting CO_2 Uptake



Natural Gas Plants

4-6%

Coal Plants

12-14%

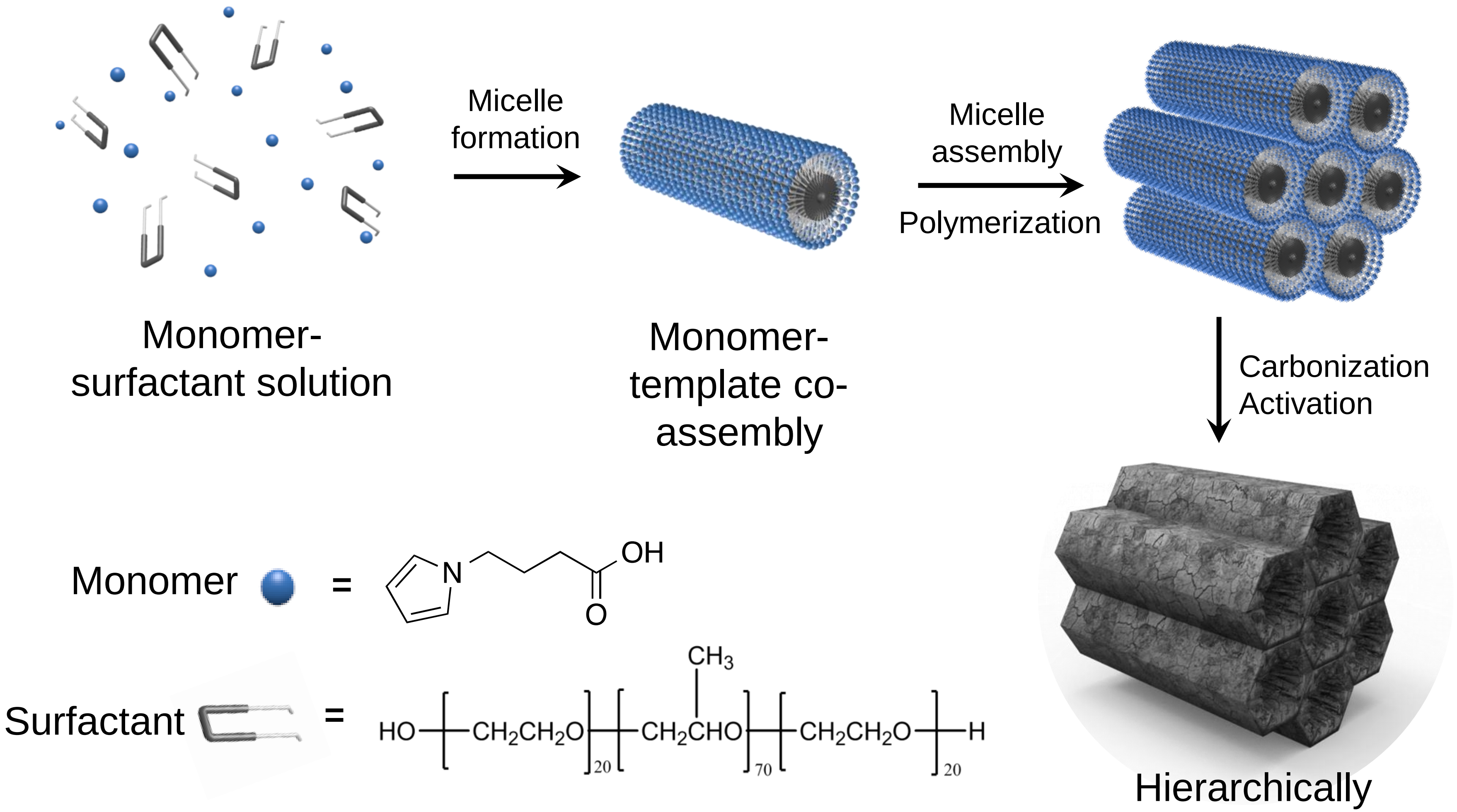
CO_2-Surface
Surface Chemistry

CO_2-CO_2
Thermodynamic

Hierarchal Carbons as a CO_2 Adsorbent

- Tunable pore sizes and distribution
- Optimal heat properties
- High surface area and pore volume
- Flexibility on surface functionalization
- Physical adsorption – not chemical
- Chemical stability
- Earth-abundant and low cost

Soft-Template Synthesis



Micelle formation

Micelle assembly

Polymerization

Monomer-surfactant solution

Monomer-template co-assembly

Carbonization
Activation

Hierarchically porous carbon

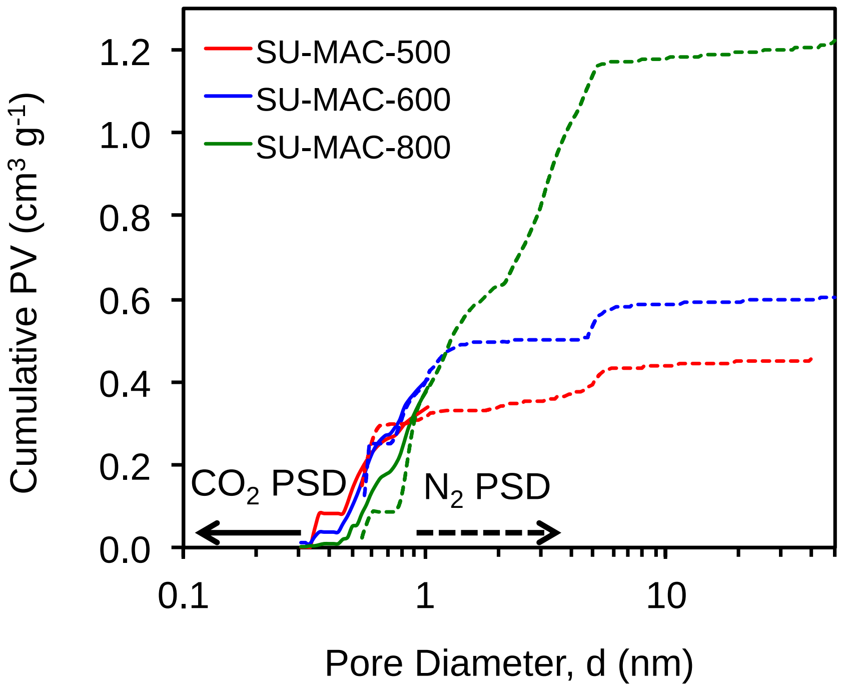
Monomer =

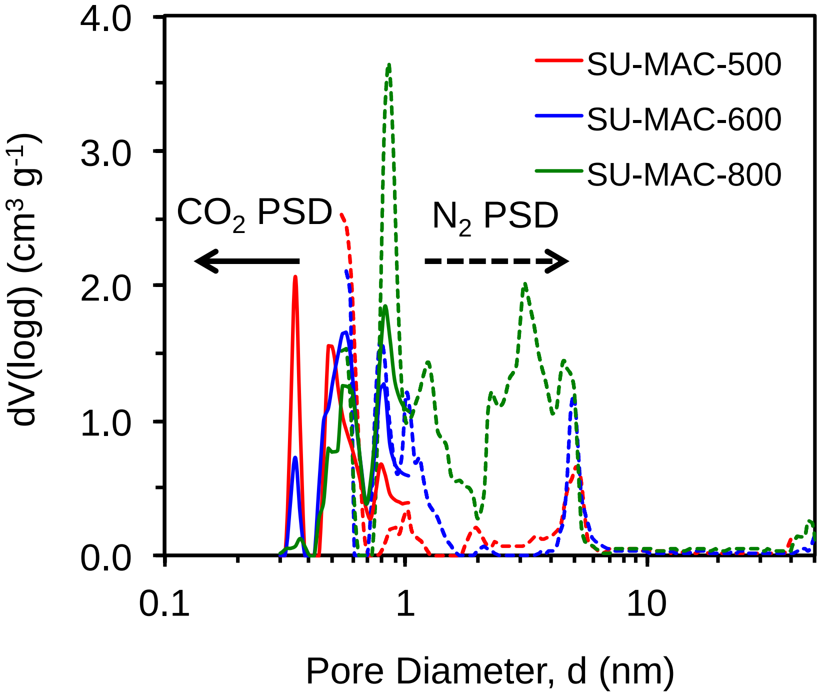
Surfactant =

$$HO-\left[CH_2CH_2O\right]_{20}-\left[CH_2\overset{CH_3}{C}HO\right]_{70}-\left[CH_2CH_2O\right]_{20}-H$$

PEO-PPO-PEO

Pore Analysis – Pore Size Distribution (PSD)



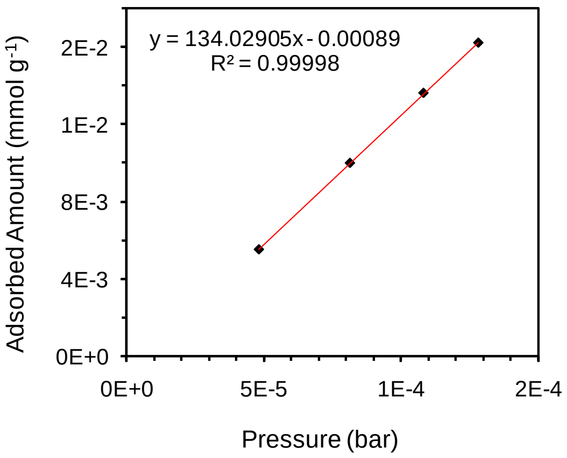


- BET surface area (SU-MAC-500, 600, 800): 942, 1500 and 2369 m^2 g^{-1}
- Higher act. temperature ➔ higher surface area and total pore volume

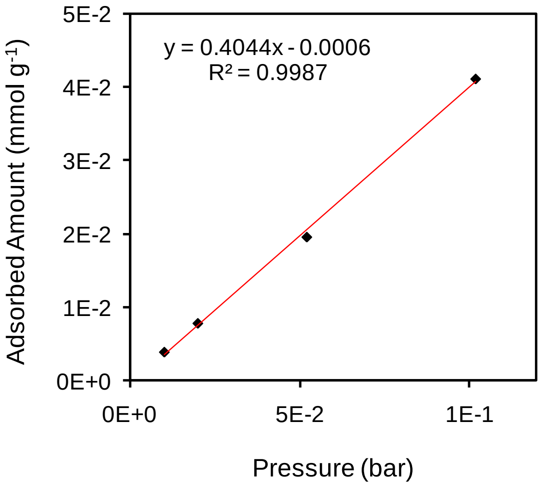
Henry's Law CO_2/N_2 Selectivity

SU-MAC-500

CO_2 initial slope



N_2 initial slope

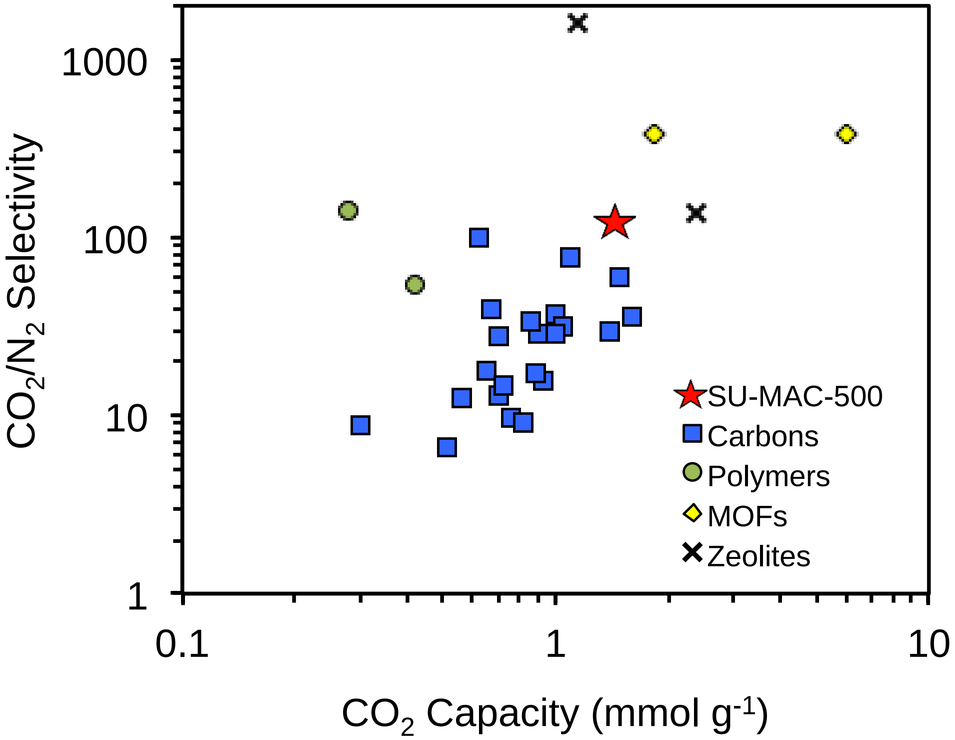


Sample	CO_2 Capacity (mmol g^{-1})			N_2 Capacity (mmol g^{-1})	CO_2/N_2 Selectivity
	273 K	298 K	323 K	298 K	
SU-MAC-500	6.03	4.50	3.06	0.39	331:1
SU-MAC-600	6.49	4.18	2.54	0.37	54:1
SU-MAC-800	5.20	3.11	1.88	0.37	12:1

Literature Selectivity for AC

Activated Carbon	CO_2 Capacity 25 C, 1 bar (mmol/g)	CO_2/N_2 Selectivity	Reference
CP-2-600	3.9	5.3	Sevilla et al. Adv. Funct. Mater. 2011
AS-2-600	4.8	5.4	Sevilla et al. Energy Environ. Sci. 2011
VR-93-M	4.2	2.8	Wahby et al. ChemSusChem 2010
CN-950	4.3	30	Ma et al. J. Mater. Chem. 2013
NPC-650	3.1	12.5	Wang et al. J. Mater. Chem. A 2013
NG-7	2.7	9.1	Kemp et al. Nanotech. 2013
Bamboo-1-973	4.0	11.1	Wei et al. ChemSusChem 2012
Petro. Coke	3.5	5.1	Hu et al. Environ. Sci. Technol. 2011
Polypyrrole	4.3	15.9	Chandra et al. Chem. Commun. 2012
Polyfurfuryl alcohol	3.2	6.5	Sevilla et al. J. Colloid Interface Sci. 2012
SU-MAC-500	**4.5**	**331**	**This work**

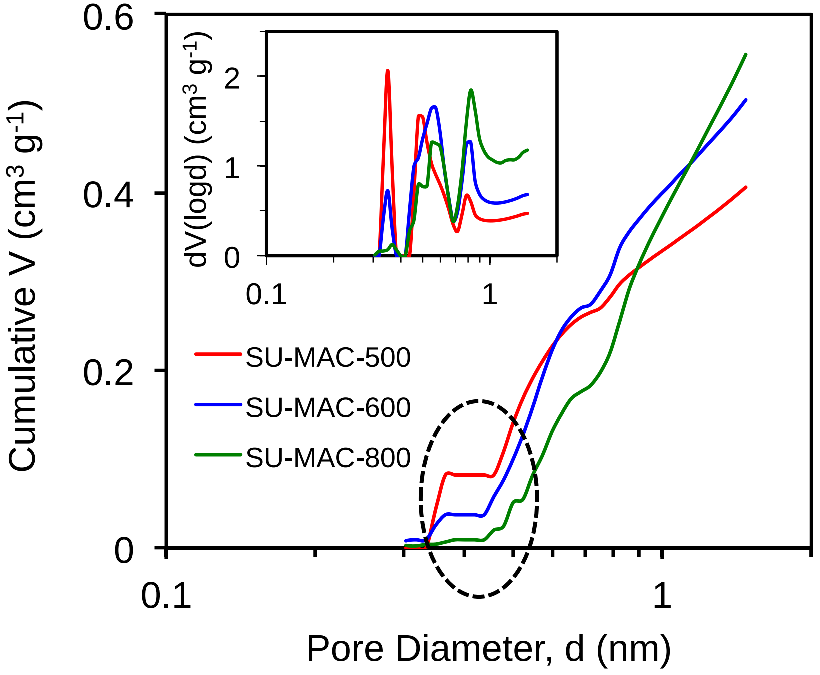
Comparison of CO_2 Capture Potential



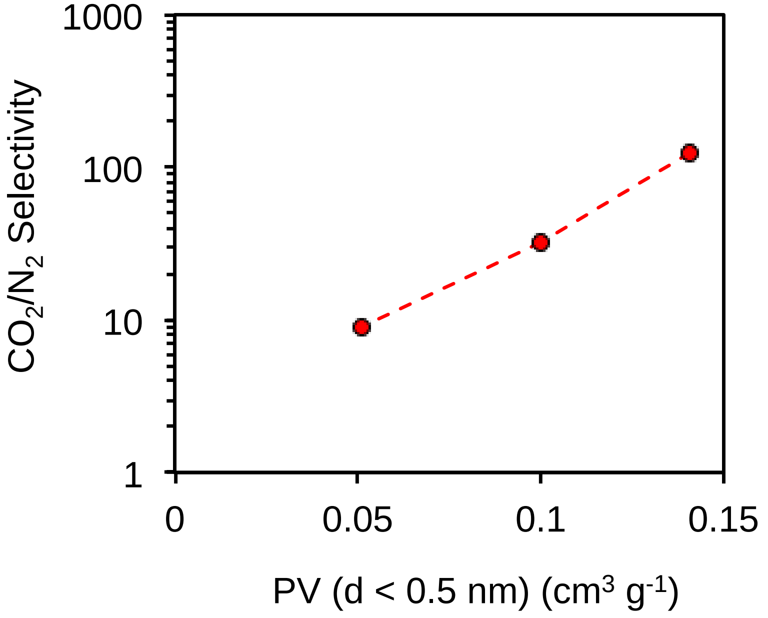
(1) Wei et al. Adv. Funct Mater. 2013. (2) Hao et al. J. Am. Chem. Soc. 2011. (3) Chandra et al. Chem. Comm. 2012. (4) Xiang et al. Nat. Commun. 2012. (5) Ma et al. J Mater Chem A 2013. (6) Patel et al. Adv. Funct.l Mater. 2013. (7) Patel et al. Nat Commun 2013.

Factors Affecting Selectivity: Ultra-Microporosity

PSD by DFT method (CO_2 @273 K)



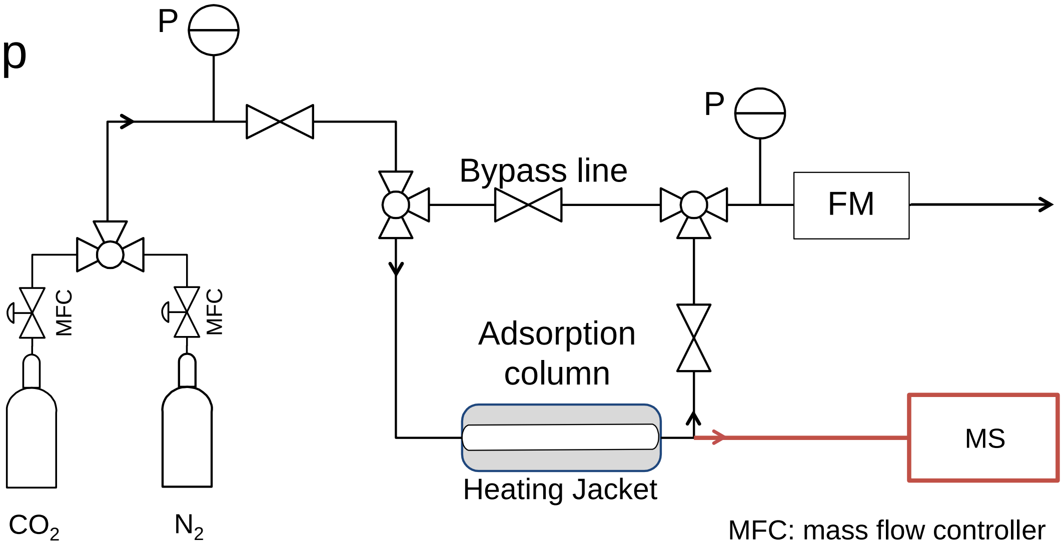
Correlation of selectivity vs. PV (d < 0.5 nm)



- Decreased ultra-small pore volume with increasing activation temperature
- Enhanced CO_2 adsorption potential in narrow pores

Dynamic Column Breakthrough

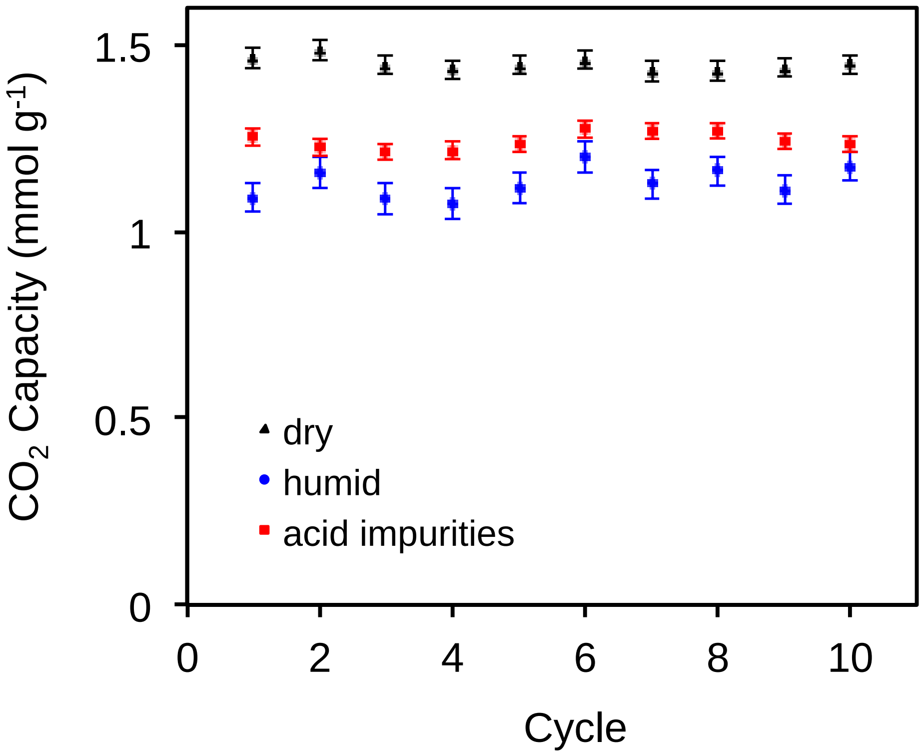
Experimental Setup



MFC: mass flow controller
P: pressure gauge
FM: flow meter
MS: mass spectrometer

- 10% CO_2 + 90% N_2, 1 bar and 298 K
- Humidity and acidic impurities added to simulate various coal flue gases

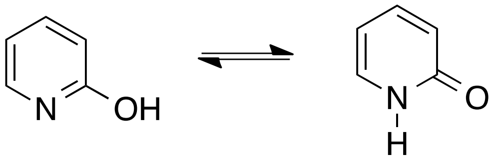
Cyclability



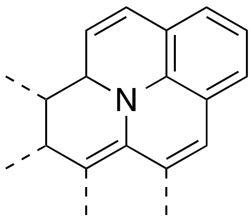
- Regeneration: N_2 purge at 25 ° C (dry)
- 10 cycles: fully recovered CO_2 capacity
- Excellent cyclability

Effect of Nitrogen Functionalities

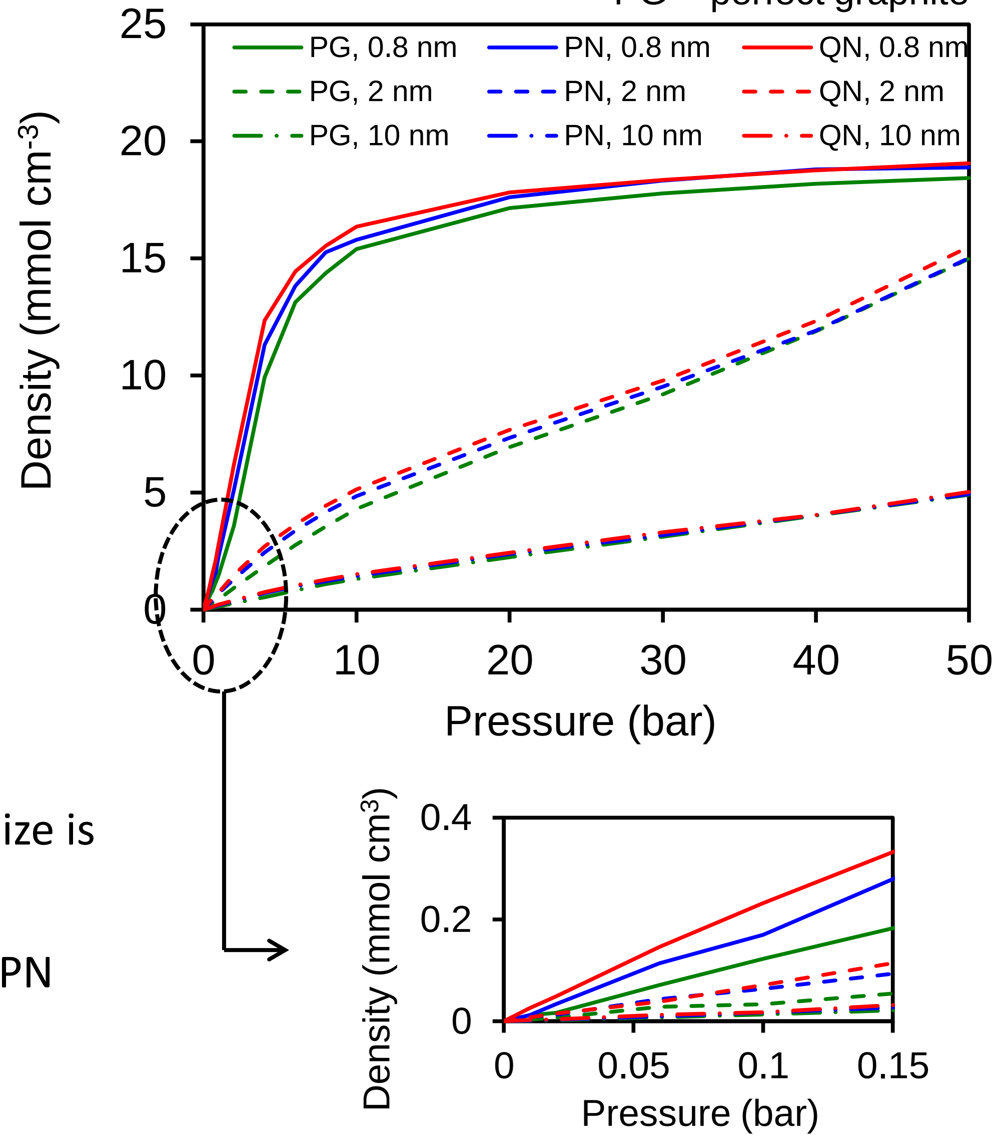
Pyridonic nitrogen (PN)



Quaternary nitrogen (QN)

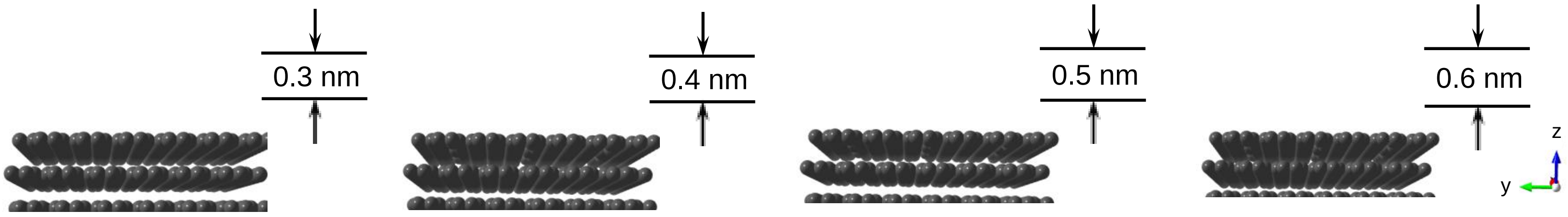


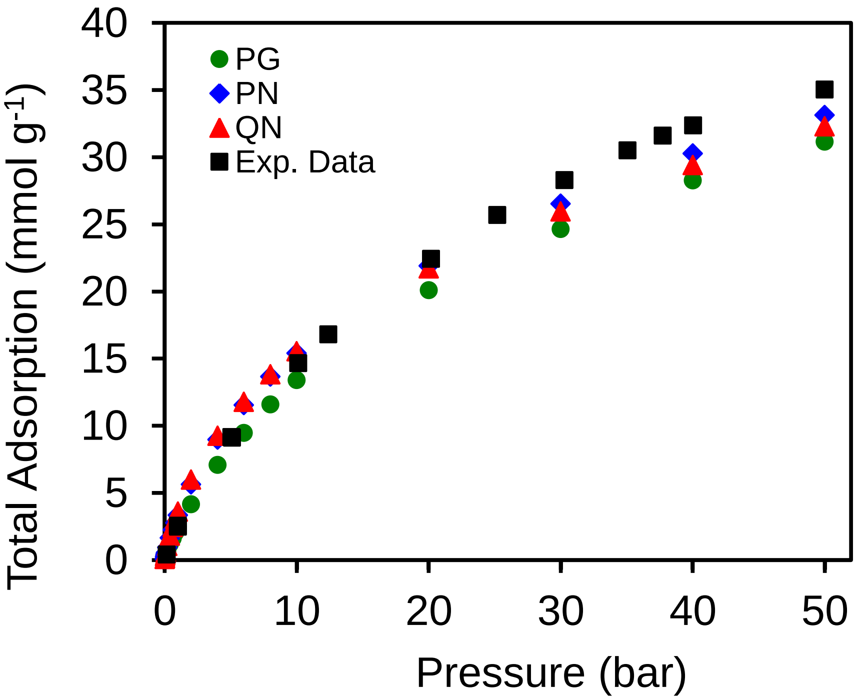
*PG = perfect graphite



- N enhances CO_2 uptakes when pore size is small and/or at low pressure
- QN leads to higher CO_2 uptakes than PN

GCMC Simulations versus Experiments





Major Findings

- Hierarchal nitrogen-doped porous carbon was made with designed pyrrole monomer via a soft-templating approach
- Promising CO_2 capture capacity and CO_2/N_2 selectivity
- Selectivity as a function of the pore size and nitrogen functionalities
- Potential in post-combustion capture (cyclability, regeneration requirements, stability towards moisture and acidic impurities, etc.)
- Computational modeling can serve as an excellent screening tool for new sorbent design

Acknowledgements

GCEP

Global Climate & Energy Project
STANFORD UNIVERSITY